

FIG. 2. Dependence of photoconductivity on the beam current of SR as a function of irradiation time.

Moreover, if $N_{\text{ind}}(t)$ is larger than initial defect density in the films, we obtain an inverse proportional relationship between σ_{ph} and t as follows:

$$\sigma_{\text{ph}} \propto (N_{\text{Si}} L \eta t)^{-1}. \quad (4)$$

This relationship can explain the results in Fig. 2 in terms of $\sigma_{\text{ph}} \propto t^{-1}$ and $\sigma_{\text{ph}} \propto L^{-1}$. The direct bond-breaking process is a principal mechanism for the degradation of *a*-Si:H induced by SR light irradiation. However, at present, the origin of the defects which determine the value of N_{Si} has been unknown.

In summary, we have examined the degradation phenomena in the *a*-Si:H films induced by the irradiation with (VUV) light produced by SR. Photoconductivity of the films rapidly decreases in a few seconds and is inversely proportional to both the irradiation time and light intensity. A principal mechanism of the degradation is proposed.

We wish to thank the staff of UVSOR section in the Institute for Molecular Science for the support of the experimental instruments. We are also grateful to H. Ohashi and O. Yamaoka of Toyohashi University of Technology for their technical assistance. This work is supported by a Grant-in-Aid for Scientific Research on Priority Areas from The Ministry of Education, Science and Culture of Japan.

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Thermal reaction of Al/Ti bilayers with contaminated interface

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(Received 23 May 1988; accepted for publication 14 November 1988)

We have studied some new aspects of thermal reactions in Al/Ti bilayers in which the interface is purposely contaminated with oxygen. After annealing at a temperature of 460 °C, an Al_3Ti compound forms at the interface, moreover some Al diffuses through the Ti to form a compound at the free surface. The amount of aluminum at the free surface can be as large as at the interface. Nucleation and lateral growth of Al_3Ti at the interface are locally unfavorable. This results in a competition between the lateral growth of Al_3Ti at the Al/Ti interface and the diffusion of Al to the free surface. Once full coverage by Al_3Ti is obtained at the Al/Ti interface, the diffusion of Al to the surface becomes negligible.

In experiments on thermal annealing of metallic bilayers, it is often very difficult to assess the role of contamination on the reactions observed. This is particularly true for Al/Ti bilayers. Significant differences exist between the reported values of the activation energy of formation for the Al_3Ti phase growing at the interface.¹⁻⁷ The high reactivity of Al and Ti with oxygen is probably related to these incon-

sistencies. It has been shown recently that in bilayers consisting of an Al film with an overlaid Ti film ("Al/Ti") whose interface has been purposely contaminated, some Al diffuses through the overlying titanium and forms a compound at the surface. In addition, an aluminide layer also forms at the interface. Only the interfacial compound forms in samples that are not purposely contaminated.⁸ Such a preferential

nucleation at the free surface has also been observed in the reaction of metal films with a silicon substrate.⁹

In this communication, we show that interfacial oxygen influences the nucleation and growth of the reacted layers at both the interface and the surface of the Ti layer. We propose a model to explain the relation between the morphology of the aluminide at the interface and the formation of a compound layer at the free surface.

The substrates used in this work are Si $\langle 111 \rangle$ wafers on which a SiO_2 oxide is thermally grown. The deposition system is an *e*-beam evaporator with an oil-free pump. The base pressure is about 5×10^{-8} Torr and pressures of at most 10^{-6} and 6×10^{-7} Torr are maintained during evaporation of Al and Ti, respectively. To contaminate the interface after the Al film is deposited, we introduce air at a pressure of 1 atm and wait for a duration of 1 s–5 min to oxidize the freshly deposited aluminum layer. An estimated equivalent of 1–4 nm of Al_2O_3 (Ref. 10) forms on the Al surface. The chamber is then again pumped down to 5×10^{-8} Torr, whereupon Ti is evaporated first on a shutter to getter the residual gas and then on the Al film. In all our samples, Ti is on top of Al; this is inverse to the samples used in all previously cited experiments.

The as-deposited samples are isothermally annealed at temperatures ranging from 400 to 550 °C for 15–420 min. To obtain reproducible results, it is important that the samples be transferred in a few minutes from the evaporation chamber to the vacuum annealing furnace, and annealed within a few hours. The pressure in the vacuum annealing furnace is about 2×10^{-7} Torr. To further decrease the oxygen residual pressure, the samples are wrapped in Ti foils.^{6–8}

Some of the samples have been studied by cross-sectional transmission electron microscopy. Figure 1(a) is a cross-section micrograph of an as-deposited contaminated $\text{SiO}_2/\text{Al}/\text{Ti}$ sample. Figure 1(b) shows an identical sample after less than 5-min vacuum annealing at 460 °C. Indentations are visible at the interface. Similar interfacial indentations have been observed in thermal reactions of Si/metal structures.¹ The Al_3Ti phase is clearly identified in those indentations by electron diffraction. The orientation of the Al_3Ti phase is related to the orientation of the Al grains in which the compound penetrates. The nucleation does not seem to occur preferentially at Al grain boundaries. We can, however, be misled in our interpretation by the fact that Al grains grow with annealing time. The Al_3Ti phase is embedded into the Al layer. Among the possible interpretations is that Ti and not Al is the dominant moving species in the formation of these indentations. Figure 1(c) shows a cross-sectional transmission electron micrograph of a contaminated sample following heat treatment at 460 °C for 30 min. In contrast to the sample annealed for 5 min [Fig. 1(a)], precipitates are clearly visible at the surface (arrow). It would be helpful for completeness to have corresponding micrographs of samples without any contamination with a Ti overlayer. This condition is very difficult to meet. Instead, we rely on micrographs of bilayer samples with the Al at the top. Micrographs for such presumably clean $\text{SiO}_2/\text{Ti}/\text{Al}$ samples have been published by Wittmer, LeGoues, and Huang⁵ for samples annealed for $\frac{1}{2}$ -h annealing at 450 °C. The picture reveals a com-

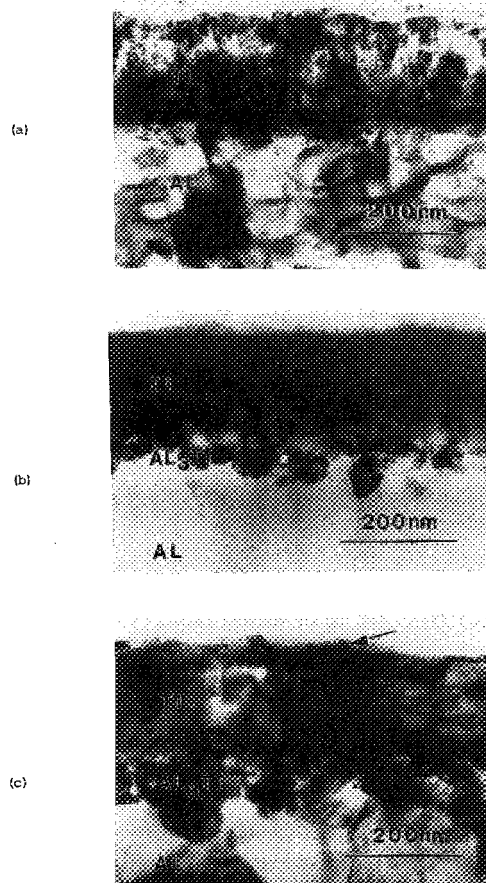


FIG. 1. Transmission electron microscopy of cross sections of $\text{SiO}_2/\text{Al}/\text{Ti}$ samples (a) as deposited, (b) after thermal anneal at 460 °C for 5 min, and (c) after 30-min thermal anneal at 460 °C.

plete coverage of the Ti interface by the Al_3Ti compound.

The result of Fig. 1 can be qualitatively understood if we model the interfacial zone as a very thin buried oxide film separating the Al and Ti layers as schematically represented in Fig. 2. We can then interpret the transmission electron micrograph and posit that (i) the oxide retains its integrity during thermal annealing and that (ii) Al_3Ti poorly wets the oxide layer.¹² (Usually a metal wets a metallic substrate more easily than a very stable oxide substrate.) This second postulate is derived from the observation that the contact

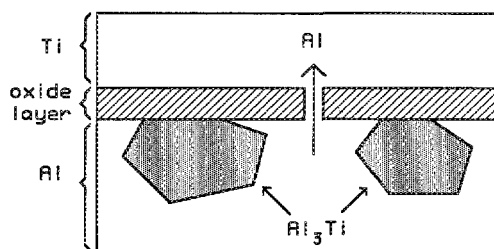


FIG. 2. Schematic model depicting the effect of an oxide interface on the reaction between Al and Ti. The Al_3Ti phase nucleates heterogeneously at the Al/oxide interface. Al_3Ti does not wet the oxide. At places where nucleation does not take place, Al can diffuse through the oxide and into Ti.

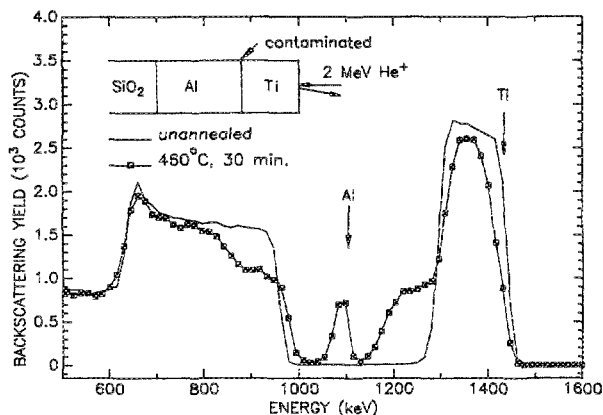


FIG. 3. 2-MeV He^+ backscattering spectra of an Al (600 nm)/Ti (200 nm) bilayer with contaminated interface before (line) and after (squares) 30-min annealing at 460 °C (beam incidence: normal; scattering angle of detected particles: 170°).

angle of Al_3Ti with the interface is larger than 90° (see Fig. 1). According to classical nucleation theory,¹³ the work in forming a nuclei of critical size of a new phase on a substrate which is not wetted is higher than on a substrate which is wetted. Moreover, during their growth, the grains try to minimize their surface free energy and the lateral growth is hindered. These features are indeed all observed in Figs. 1(b) and 1(c).

Besides the structure of the interfacial Al_3Ti layer, the presence of oxygen at the Al/Ti interface also changes the Al transport. In Fig. 1(c), we observe a compound at the surface after 30-min vacuum annealing at 460 °C. This compound is identified by electron diffraction as Al_3Ti , with possibly also some Al, and is present only if the interface is purposely contaminated with oxygen.⁸ To look at the transport of Al in a quantitative way, several samples have been annealed for 30 min at 460 °C and characterized by ^4He backscattering spectrometry. The only intentional difference between these samples was the degree of contamination at the interface. As many of the other parameters as possible (evaporations rates, thicknesses, residual pressures, wrapping) were kept fixed in this experiment to minimize the variables. Figure 3 shows typical ^4He backscattering spectra of contaminated SiO_2/Al (600 nm)/Ti (200 nm) samples before and after 30-min annealing at 460 °C. A clear step is visible at the signal position of surface Al for the annealed samples. A 200-nm-thick Al_3Ti layer forms at the Al/Ti interface.

In Fig. 4, we plot for different "contaminated" samples annealed at 460 °C during 30 min the "total amount of Al transported" beyond the $\text{Al}_3\text{Ti}/\text{Ti}$ interface (expressed in units of equivalent pure Al thickness). This quantity defined as the sum of the Al contained in the unreacted titanium layer plus the Al at the surface derived from the backscattering spectra of the samples as function of the Al_3Ti interfacial thickness. We observe a correlation between the thickness of the aluminide at the interface and the aluminum that diffuses further into the Ti film. The trend is a decrease in the total amount of aluminum that diffuses beyond the $\text{Al}_3\text{Ti}/\text{Ti}$ interface with increasing thickness of the interfacial Al_3Ti .

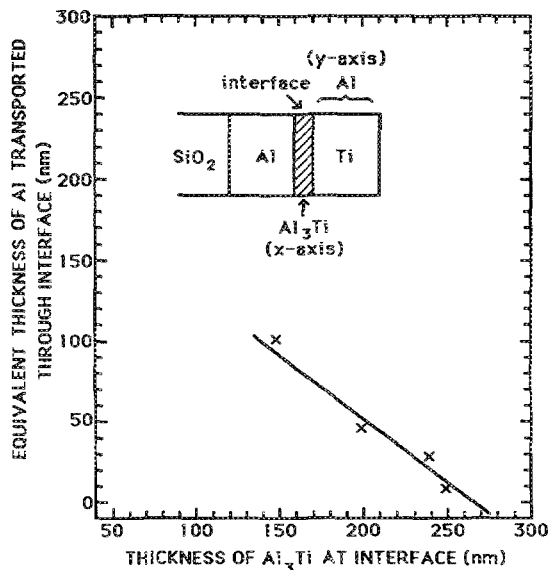


FIG. 4. "Total amount of Al transported" beyond the $\text{Al}_3\text{Ti}/\text{Ti}$ interface, defined as the sum of the Al contained in the unreacted titanium layer plus the Al at the surface for different "contaminated" samples annealed at 460 °C during 30 min, as a function of Al_3Ti thickness at the interface. This amount is expressed in units of equivalent pure Al thickness. Except for the degree of contamination at the original Al/Ti interface, the preparation (deposition rates, thickness, vacuum) and annealing (wrapping, residual pressures) were kept as similar as possible.

This result can be understood as follows. There is a competition between the lateral growth of the Al_3Ti layer and the diffusion of aluminum through the oxide as depicted in Fig. 2. The more Al_3Ti builds up at the interface, the less aluminum diffuses into the remaining unreacted titanium, or moves to the surface. The aluminide compound, as it grows, restricts the diffusion paths for aluminum. Once complete coverage is achieved, the flow of aluminum to the free surface stops and the Al transported to the interface is consumed to grow the aluminide interfacial layer. Kinetics data obtained by backscattering spectrometry are consistent with this model; annealing the samples for long times essentially increases only the thickness of the interfacial Al_3Ti layer. This model is consistent with previous observations by Zhao, So, and Nicolet which shows that oxygen at the free surface also hinders the nucleation of Al_3Ti at the free surface.⁷

In conclusion, thermally induced nucleation and lateral growth of the Al_3Ti at the interface of an Al/Ti bilayer are less favorable when the Al is contaminated during deposition than in the case of a clean Al/Ti interface. Apparently, oxide at the interface does not suppress the diffusion of Al or Ti. The diffusion of Al into the Ti and the subsequent growth of an Al_3Ti compound layer at the free surface occurs as long as complete coverage of Al_3Ti at the Al/Ti interfacial region is not achieved. In a presumably clean sample, this occurs in a time duration that does not allow significant amounts of Al to diffuse to the surface so that no Al signal from the sample surface in the backscattering spectra is detected.

We believe that the new growth mechanism described here is general and applies to other contaminated systems too, provided the reaction occurs at a temperature for which

the diffusivity of one species into the other is comparable or larger than its diffusivity in the interfacially growing compound.

Technical assistance from Rob Gorris and Bart Stevens is gratefully acknowledged. The financial support was provided in part by the Office of Naval Research under Contract No. N000 14-84-K-0275. We also thank the Swiss National Science Foundation for a fellowship to one of us (M. Thuillard).

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Room-temperature observation of impurity states in bulk GaAs by photoreflectance

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(Received 11 July 1988; accepted for publication 15 November 1988)

Photoreflectance (PR) experiments are performed on thick GaAs/GaAs epitaxial layers and on a nearly perfect GaAs single crystal. The first observations of PR spectra induced by impurities (shallow acceptors) in bulk semiconductors like gallium arsenide are reported.

Photoreflectance (PR) spectroscopy has recently been demonstrated as a valuable method for the characterization of compound semiconductors, heterostructures, and multiple-quantum wells (MQW).^{1,2} Alloy composition, quantum-well width, and interfacial quality of MQW may be controlled by this technique, but practically nothing is known about the possibilities of PR for investigations of impurity states in semiconductors.

A weak peculiarity at long wavelengths in the spectrum of a MQW has been observed recently at a low temperature by Shanabrook, Glembocki, and Beard.³ Comparing these facts with the photoluminescence excitation spectrum measured at $T = 6$ K the authors suggested that this peak is caused by shallow donors. Some long-wavelength oscillations have been observed in the thin epitaxial layers of p -type $\text{Al}_x\text{Ga}_{1-x}\text{As}$ grown by molecular-beam epitaxy on (100) GaAs substrates.⁴ These oscillations associated with an impurity were registered in the $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ structures with $x > 0.15$, but not in GaAs.

In this communication we report the first clear observations of photoreflectance spectra induced by impurities (probably shallow acceptors) in bulk semiconductors like high-quality gallium arsenide.

The experimental technique for photoreflectance is similar to that discussed in Ref. 5. The modulating beam from

an Ar-ion laser ($\lambda = 514$ nm) passes through a chopper onto the sample. A monochromatized beam from a tungsten lamp is reflected by the sample at near-normal incidence (about 5°) to a Si detector. The modulated reflectivity spectrum is detected by standard phase-locked techniques. The intensity of the pump beam is from 0.1 to 200 mW/cm².

Two types of samples are used in this study: (1) thick ($d \geq 10$ μm) epitaxial GaAs layers grown by vapor-phase epitaxy doped with Te to $n = (0.5-2) \times 10^{17}$ cm⁻³ on a (100) GaAs substrate and (2) pure undoped (100) GaAs single crystal. The two-crystal x-ray diffraction measurements did not show any inhomogeneities in the single crystal. The half-width of the 400-diffraction peak was less than 17 arcsec. Synchrotron x-ray topographs made at the Hamburger Synchrotronstrahlungslabor did not show any defects, either.

Typical PR spectra for both types of samples are presented in Fig. 1. The classical Franz-Keldysh oscillations are observed in Fig. 1(a) at $\hbar\omega > E_g$ for an n -type GaAs epilayer with $n = 10^{17}$ cm⁻³. The spectrum in Fig. 1(b) (the details of which are presented in Fig. 2, but with higher modulating power) is quite different and more interesting. The very sharp peaks having a half-width of about 6 meV (i.e., less than kT) are seen near the energy gap of GaAs. This part of the spectrum is nearly the same as that of the room-temperature electrolyte-electroreflectance spectrum measured from undoped n -GaAs with a small dc applied bias voltage.⁶ The main PR peak is observed at the energy of 1.409 eV which is

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